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Calorimetric study of solvation of low polar solutes in propylene glycol and methyl cellosolve at 298 K

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ABSTRACT

Enthalpies of solution of low-polar substances: aliphatic and aromatic hydrocarbons, including alkanes, cycloalkanes, alkylbenzenes, and halobenzenes in two solvents, propylene glycol and methyl cellosolve, were measured at temperature T = 298.15 K using titration calorimetry. In addition, the enthalpies of solution of poorly soluble solid solutes, naphthalene and biphenyl, in these solvents were determined using indirect method by measuring the enthalpies of solution of liquid mixtures containing them. The enthalpies of solvation from the gas phase were calculated from these data.

The enthalpies of solvation in propylene glycol and methyl cellosolve and previously reported enthalpies of solvation in ethylene glycol were correlated with each other and with molecular parameters of solutes.

1. Introduction

Methyl cellosolve (2-methoxyethanol, $CH_3OCH_2CH_2OH$, further MC) and propylene glycol (1,2-propanediol, $CH_3CH(OH)CH_2OH$, further PG) are two structural isomers and two important industrial solvents [1]. Methyl cellosolve is used as a solvent in dye and rubber industries, production of cellulose acetate films and laboratory organic synthesis. MC is a toxic compound which can be converted by alcohol dehydrogenase into methoxyacetic acid which can enter the Krebs cycle [2]. In contrast, PG has a very low toxicity for humans.[3] Thus, it is used as a solvent for pharmaceuticals and in food industry, as well as in rubber and polymer production, and as a component of automotive antifreeze. Both MC and PG molecules differ by a methyl group from a molecule of another common industrial solvent, ethylene glycol (1,2-ethanediol, $HOCH_2CH_2OH$, further EG).

The solvent effect on equilibria in chemical reactions, solubility, interfacial distribution properties of dissolved compounds is governed by the Gibbs free energy change. The enthalpy of solvation (transfer of solute from the gas phase into solvent) determines the dependence of the Gibbs energy of solvation on temperature according to Van't Hoff equation. Despite a broad practical use of PG and MC, thermodynamic functions of solvation or solution in these solvents are almost not studied.

Our special interest is the solvophobic effect in self-associated solvents and its influence on the solvation properties. Both MC and PG are self-associated due to intermolecular hydrogen bonds. In our previous papers [4–6] we developed a methodology to describe the solvophobic effect in various solvents on the basis of the values of Gibbs free energy and enthalpy of solvation for low-polar solutes. Thus, in this work we have selected a number of such solutes to determine their enthalpies of solution in PG and MC.

Calorimetric measurement of the enthalpies of solution for non-polar solutes in PG is complicated by their low solubility, low speed of dissolution, and a high viscosity of solvent. No values of the enthalpies of solution of hydrocarbons and their halogenated derivatives in PG were found in literature. The solubility of hydrocarbons in MC is higher, but the calorimetric data for their solutions are also very limited.

In the present work, novel thermodynamic data for solutions of hydrocarbons and their halogenated derivatives in PG and MC at infinite dilution and T = 298 K are obtained using titration calorimetry technique.

2. Experimental

2.1. Materials and methods

Propylene glycol and methyl cellosolve with purity >0.99 were purchased from Acros Organics. All the solutes were at least 0.99 pure grade from Sigma–Aldrich, Acros and Fluka. They have been used without further purification. The absence of significant

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